

# $^{63,65}\text{Cu}$ NMR and NQR evidence for an unusual spin dynamics in $\text{PrCu}_2$ below 100 K

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We report the results of a  $^{63,65}\text{Cu}$  NMR/NQR study probing the intermetallic compound  $\text{PrCu}_2$ . The previously claimed onset of magnetic order at 65 K, indicated in a  $\mu\text{SR}$  study, is not confirmed. Based on our data we discuss different possible reasons for this apparent discrepancy, including a non negligible influence of the implanted muons on their environment. Competing dipolar and quadrupolar interactions lead to unusual features of the magnetic-ion/conduction-electron system, different from those of common intermetallics exhibiting structural or magnetic instabilities.

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## I. INTRODUCTION

The Van Vleck paramagnet  $\text{PrCu}_2$  exhibits peculiar electronic and magnetic properties, whose complete understanding is still to be achieved. The  $4f$  electron ground-state multiplet of the  $\text{Pr}^{3+}$  ions is split into nine singlets by the crystal electric field. Nevertheless, an induced Jahn-Teller (JT) transition is observed at  $T_{\text{JT}} = 7.6$  K,<sup>1,2</sup> where the crystal structure changes from orthorhombic to slightly monoclinic.<sup>3,4,5</sup> An incommensurate antiferromagnetic (AF) order below  $T_N = 54$  mK among the Pr nuclear magnetic moments was claimed on the basis of magnetic susceptibility, specific heat, and neutron scattering measurements.<sup>4,6</sup> The respective moments align along the  $a$  direction of the orthorhombic unit cell with a propagation vector  $\vec{q} = (0.24, 0, 0.68)$  in the reciprocal lattice. Magnetization and susceptibility measurements indicate a large polarization of the  $4f$  Pr magnetic-moments in the presence of an external field.<sup>7,8</sup> At low temperatures the easy and hard magnetization axes are along the  $a$  and  $c$  direction, respectively. Quite surprisingly the two magnetization axes are exchanged for fields exceeding 10 T, leading to a metamagnetic transition.<sup>7,8</sup> The  $4f$  electron Pr-quadrupole moments play an important role in the physics of  $\text{PrCu}_2$ . In particular the JT transition is ascribed to a phonon-mediated interaction between the quadrupole moments,<sup>3</sup> whereas the metamagnetic transition has been ascribed to a change in the orientation of the spatial charge distribution.<sup>9</sup>

Based on the results of a muon spin resonance ( $\mu\text{SR}$ ) study, AF ordering of the localized Pr  $4f$  electron moments below 65 K has recently been suggested.<sup>10</sup> Since such a magnetic transition in this temperature region is not reflected in the results of either neutron scattering or susceptibility experiments,<sup>3,4,7</sup> it may be assumed

that the inferred magnetic order does not involve long-range order and static internal fields. Considering the electronic configuration of the  $\text{Pr}^{3+}$  ions, the above result is really unexpected and calls for additional checks. Since the  $\mu\text{SR}$  results may be due to dynamically-induced non vanishing internal fields, it is important to use a microscopic technique for investigating the phenomenon further. In this paper we report a systematic study of  $\text{PrCu}_2$  by means of Cu-based nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) experiments between 4.2 K and room temperature.

## II. EXPERIMENTAL

Nuclear resonance measurements were made using standard spin-echo techniques employing a phase-coherent pulsed spectrometer.  $^{63,65}\text{Cu}$  NMR and NQR spectra were collected by measuring the integrated spin-echo signal as a function of the exciting radio-frequency (RF) in fixed external magnetic fields. The spin-lattice relaxation rate (SLRR)  $T_1^{-1}$  was measured by destroying the  $z$ -component of the equilibrium nuclear magnetization by means of a short RF pulse and monitoring its recovery as a function of a variable delay between this preparation pulse and a spin-echo sequence. The spin-spin relaxation rate (SSRR)  $T_2^{-1}$  was obtained from the  $\tau$  dependence of the signal after a  $\pi/2 - \tau - \pi$  sequence.

Single crystalline  $\text{PrCu}_2$  samples were grown at Osaka University by means of the procedure described in Ref. 11. Since the system is metallic, the NMR signal from the single crystal is very small because the penetration depth of the RF pulses is of the order of 1  $\mu\text{m}$  only. We observed an unexpected splitting and broadening of the NMR lines, which we traced back to a non-perfect orientation of the applied magnetic field with respect to

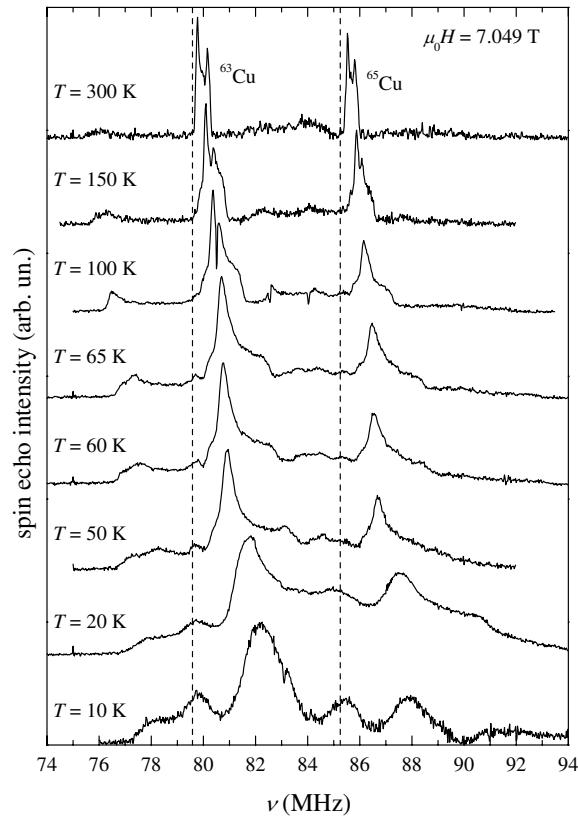


Figure 1:  $^{63,65}\text{Cu}$ -NMR powder spectra of  $\text{PrCu}_2$  at selected temperatures and in a field of 7.049 T. The vertical dashed lines mark the reference NMR frequencies for the two Cu-isotopes.<sup>12</sup>

one of the crystalline axes of the sample. From a detailed analysis we concluded that meaningful NMR measurements on a single crystal of  $\text{PrCu}_2$  require a precision in sample orientation that is much better than  $\pm 1^\circ$ , which could not be achieved with our experimental set-up. For this reason we powdered the single-crystalline sample which not only served to avoid the orientation problem but also helped to enhance the NMR signal.

### III. NMR MEASUREMENTS

Figure 1 shows the Cu-NMR spectra of  $\text{PrCu}_2$  powder at selected temperatures. The 300 K spectrum is characterized by two main features centered at 80 and 86 MHz, which are ascribed to the NMR central-line of the  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  isotopes, respectively. Both isotopes possess a  $3/2$  nuclear spin but the gyromagnetic ratio of  $^{65}\text{Cu}$  is roughly 7% larger than that of  $^{63}\text{Cu}$ . We observe no sign of any contribution from the  $^{141}\text{Pr}$  nuclei (reference frequency  $\sim 92$  MHz at 7.049 T), most probably because their extremely large hyperfine coupling<sup>6</sup> results in very short relaxation times. Both Cu NMR lines are split by  $\sim 1$  MHz. We ascribe this splitting

to a second-order quadrupolar perturbation of the Zeeman Hamiltonian. The wings observed between 75 and 90 MHz correspond to the first-order quadrupolar perturbation. These wings are more prominent at lower temperatures and it may be noted that, rather than a sharp edge, they exhibit a smooth edge suggesting, as explained below, a non-zero anisotropy  $\eta$  of the electric field gradient (EFG). With decreasing temperatures, the complexity of the spectrum increases. As may be seen in fig. 1, the asymmetry and width of the lines grows and they partially merge together. The quadrupolar wings are strongly affected as well and a large overall shift of the lines towards higher frequencies is observed, indicating a progressively increasing Knight-shift (K). The strongly asymmetric line-shape suggests a large K-anisotropy.

The very complex structure of the low temperature NMR spectra, caused by the simultaneous EFG and K anisotropies, makes a quantitative analysis of the spectra very difficult. Therefore, we keep the interpretation mostly at a qualitative level. To this end we performed several simulations of the  $^{63,65}\text{Cu}$  NMR powder-spectrum for different values of the microscopic parameters characterizing K and EFG. The simulations involve a full diagonalization of the nuclear Hamiltonian comprising the sum of the quadrupolar and the Zeeman term corrected by K. The spectrum is then obtained from the calculated transition energies and intensities, averaged over random crystal orientations in order to simulate a powder spectrum. The microscopic parameters characterizing the quadrupolar Hamiltonian are the largest component  $V_{zz}$  of the EFG and the anisotropy  $\eta$  in the  $xy$  plane. The parameters describing K are the isotropic and anisotropic components  $K_{\text{iso}}$  and  $K_{\text{ani}}$ , respectively, as well as an axial-asymmetry term  $\epsilon$ . The notation is standard and exemplified, for instance, in Ref. 13 (pages 62–64). Figure 2(a) shows the simulated spectra that we obtained by considering only an isotropic  $K_{\text{iso}} = 1.5\%$  and no quadrupolar contribution. Naturally, this spectrum consists of only one line for each isotope, slightly shifted with respect to the reference frequency. Figure 2(b) was obtained by adding an EFG with  $V_{zz} = 0.32$  a.u. and  $\eta = 0$ . It is clear that this term induces the appearance of the wing structures and a splitting of the central lines. The effect of adding a non-zero anisotropy  $\eta$  is demonstrated in figs. 2(c) and (d) where the calculations with  $\eta = 0.10$  and  $\eta = 0.20$ , respectively, are displayed. Upon enhancing  $\eta$ , the sharp edge of the wings is progressively smeared out, leading to a simulated spectrum with a shape resembling the experimental data at 300 K. The overall comparison of the experimental data with the simulations of fig. 2(b-d) suggests that the actual components of the EFG acting at the copper site in  $\text{PrCu}_2$  are of the order of  $V_{zz} = 0.32$  a.u. and  $\eta = 0.10$ , at least down to 100 K. An *ab initio* calculation in which the internal coordinates of the 12 ions in the unit cell of  $\text{PrCu}_2$  were optimized assuming the experimental lattice parameters ( $a = 4.4087 \text{ \AA}$ ,  $b = 7.0551 \text{ \AA}$ , and  $c = 7.4441 \text{ \AA}$ )<sup>5</sup> using the DMol<sup>3</sup> code,<sup>14</sup> yielded  $V_{zz} = 0.48$  a.u. and  $\eta = 0.11$ .

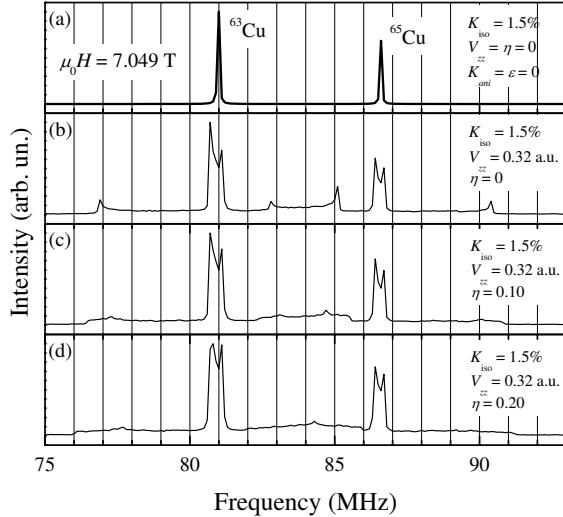


Figure 2: Simulated  $^{63,65}\text{Cu}$ -NMR powder spectra in a field of 7.049 T with  $K_{\text{iso}} = 1.5\%$  and for different values of the EFG parameters (see text).

Although the calculated absolute value of the EFG is 50% larger than that obtained by comparing experiment and simulations as described above, the direction of the dominant component of the EFG tensor is clearly established to lie in the  $bc$  plane. This is important for the discussion in section IV B.

Figure 3(b) shows a simulated spectrum where the isotropic shift of 1.5% is augmented by an anisotropic component  $K_{\text{ani}} = 1.6\%$  but no axial-asymmetry. The non-zero  $K_{\text{ani}}$  induces an asymmetric broadening of the central lines keeping rather sharp edges. The  $\epsilon$  value is responsible for the position of the maximum with respect to the edges, as shown in figs. 3(c) and (d), where the simulated spectra with  $\epsilon = 0.6$  and  $\epsilon = 2.0$  are shown, respectively.

Although these simulations allow for a qualitative description of the main features of the NMR spectra, the situation turns out to be much more complicated when we try to simultaneously take into account the influence of both EFG and K. These two contributions are indeed both non-negligible and, in principle, temperature dependent. Moreover the corresponding tensors are usually non diagonal in the crystalline-axes frame and their main frames, i.e. the frames in which the two tensors are diagonal, are not necessarily oriented along the same directions. The local symmetry of the Cu-sites provides one constraint for the EFG and K main frames. They should have one principal axis parallel to  $a$ . Concerning the orientation of the other two axes in the  $bc$  plane, nothing can be concluded from considering the crystal-structure. Therefore the angle between the K and EFG main frames in the plane is unknown. All the above considerations lead to the conclusion that the influences of both K and EFG on the spectral features cannot be regarded independently.

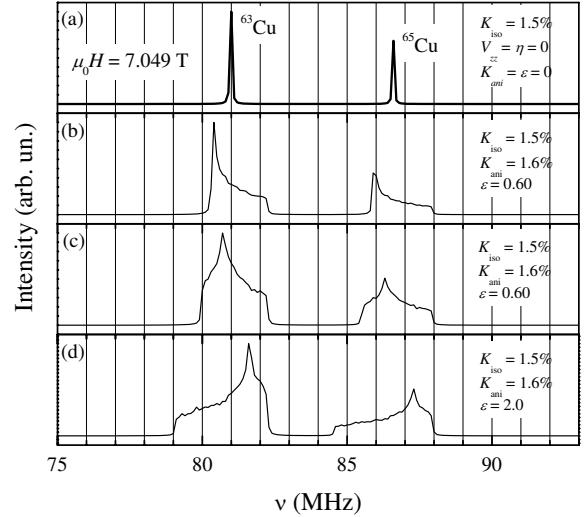


Figure 3: Simulated powder  $^{63,65}\text{Cu}$ -NMR spectra at a field of 7.049 T and for different values of the K parameters (see text).

In spite of the difficulties described above, it is still possible to extract some quantitative information from the NMR spectra shown in fig. 1. First of all, we can estimate the quadrupolar frequency  $\nu_Q$  of  $^{63}\text{Cu}$  from the widths of the wings. The data imply  $\nu_Q = 8 - 9$  MHz with no significant change upon decreasing temperature, at least down to 50 K. Inserting  $V_{zz} = 0.32$  a.u. and  $\eta = 0.10$  into the relation

$$\nu_Q = \frac{3eV_{zz}Q}{2hI(2I-1)}\sqrt{1+\eta^2/3}, \quad (1)$$

where  $Q$  is the nuclear quadrupole moment and  $I$  is the nuclear spin, we obtain  $\nu_Q = 8.3 \pm 0.8$  MHz. The second quantity that we can estimate is the largest principal component  $K_{\max}$  of the K tensor. In the presence of a K anisotropy, the spectrum adopts the typical shape displayed in figs. 3(b)-(d).<sup>13</sup> The edges of the asymmetric broadening occur at frequencies  $(1 + K_{\min})\nu_0$  and  $(1 + K_{\max})\nu_0$ , where  $K_{\min}$  is the smallest component of the K tensor and  $\nu_0$  is the reference frequency of the considered nucleus.<sup>13</sup> The position of the resonance maximum is at  $(1 + K_{\text{int}})\nu_0$ , where  $K_{\text{int}}$  is the third (intermediate) K-tensor main-component.<sup>13</sup> The temperature dependence of the high-frequency edge can be followed down to  $\sim 20$  K, thus allowing us to estimate  $K_{\max}(T)$ .

We assume that the hyperfine field  $\vec{B}_{\text{Cu}}^{\text{hf}}$  acting at the Cu-site is mainly induced by the polarization of the Pr magnetic-moments  $\vec{\mu}_{\text{Pr}}$  via an interaction mediated by the conduction electrons, such that

$$\vec{B}_{\text{Cu}}^{\text{hf}} = \vec{A}\vec{\mu}_{\text{Pr}}, \quad (2)$$

where  $\vec{A}$  is the tensor associated with the transferred hyperfine field. The orientation of one principal axis of the K tensor along the  $a$  axis and the fact that it represents

the easy magnetization direction<sup>7</sup> indicate that the maximum K component most likely lies along  $a$ , as was also suggested by our preliminary measurements on the single crystal (data not shown here). The same is implied by our estimate of  $K_{\max}(T)$ , which is found to be proportional to the susceptibility  $\chi_a(T)$  along the  $a$  axis. For a given external magnetic field  $B_0$ ,  $\vec{B}_{Cu}^{hf}$  and  $\vec{\mu}_{Pr}$  can directly be obtained from K and the susceptibility, respectively. Using eq. 2 we can calculate the diagonal term of  $\vec{A}$  along  $a$ , namely

$$A_{aa} = K_a(T)/\chi_a(T), \quad (3)$$

which is, of course, temperature independent and has a value of  $0.54 \pm 0.02$  T/ $\mu_B$ . This value is very useful in the discussion of the NQR data.

A temperature-independent  $A_{aa}$  and the fact that we do not observe significant changes of the NMR spectrum around 65 K are not compatible with an ordering of the Pr-moments at that temperature. Because of the interaction between the Pr-moments and the conduction electrons, any alignment of the Pr moments is expected to have a strong influence on the Cu NMR response.

#### IV. NQR MEASUREMENTS

##### A. Spectra

The rather large value of  $\nu_Q$  indicated by the NMR data suggests that an NQR signal can be observed in an accessible frequency range. Figure 4 shows Cu NQR spectra at selected temperatures. The recorded data reflect the expected simple NQR spectrum with one single line per isotope, reflecting the respective  $\pm 1/2 \rightarrow \pm 3/2$  transitions. The relative peak positions of the  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  signals are consistent with the nuclear quadrupole moment, which is roughly 8% larger for  $^{63}\text{Cu}$  than for  $^{65}\text{Cu}$ . From the raw data it is clear that the  $^{63}\text{Cu}$  NQR frequency is within 10% of the estimate of  $\nu_Q$  obtained from the NMR spectra. The NQR frequency increases with decreasing temperature, whereas no major changes are observed in the  $T$ -dependence of the line-widths. In order to obtain more quantitative information, we applied a best-fit procedure that is based on the frequency dependence of the intensity  $S(\nu)$  given by

$$S(\nu) = \frac{A\alpha_{65}}{(\nu - \nu_Q/\beta)^2 + (\Gamma/2)^2} + \frac{A\alpha_{63}}{(\nu - \nu_Q)^2 + (\Gamma/2)^2}, \quad (4)$$

where  $A$  is the overall intensity,  $\alpha_{65,63}$  are the natural abundances of  $^{65,63}\text{Cu}$ ,  $\nu_Q$  is the  $^{63}\text{Cu}$  NQR frequency,  $\Gamma$  is the line-width (assumed to be equal for both isotopes), and  $\beta = 1.078$  is the ratio between the quadrupolar moments of  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ . The experimental inten-

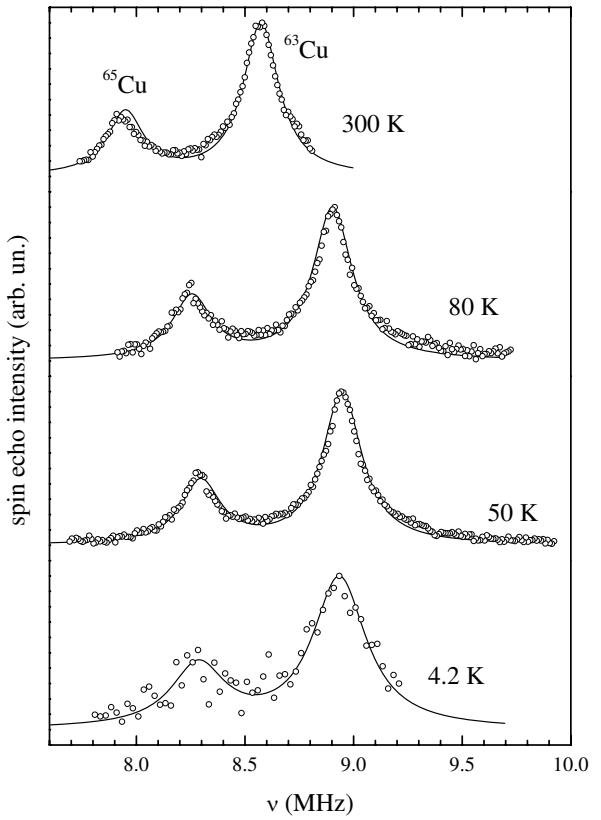


Figure 4:  $^{63,65}\text{Cu}$ -NQR spectra of  $\text{PrCu}_2$  at selected temperatures (symbols). Solid lines are best-fit curves to the data (see text).

sity  $I(\nu, T)$  is

$$I(\nu, T) = S(\nu)\nu \left[ 1 - \exp\left(-\frac{h\nu}{k_B T}\right) \right], \quad (5)$$

where the multiplicative factor  $\nu$  is due to the fact that our measurement is inductive; the term in square brackets represents the Boltzmann population factor. With this procedure, we fitted all the spectra using only  $A$ ,  $\nu_Q$ , and  $\Gamma$  as free parameters. Physically relevant are the latter two and we plot them as a function of temperature in fig. 5.

The frequency  $\nu_Q$  increases linearly with decreasing temperature down to  $T_{JT}$ , where a sudden drop in  $\nu_Q(T)$  is observed. This reflects the JT structural transition which induces a sudden change in the EFG and thus in  $\nu_Q$ . The overall change of  $\nu_Q$  between 300 K and 20 K is about 5%. Since  $\nu_Q$  is related to both  $V_{zz}$  and  $\eta$  by means of eq. 1, it is not possible to sort out whether the observed change in  $\nu_Q$  is to be ascribed to  $V_{zz}$ , or  $\eta$ , or both. Nevertheless, if we assume a constant  $V_{zz}$ , the  $\nu_Q(T)$  values imply that the anisotropy should change from  $\eta \sim 0.10$  at 300 K to approximately 0.60 at 20 K. Such a dramatic change in the asymmetry is very unlikely because it would require a strong modification of the electronic density, which does not seem to be compatible with the

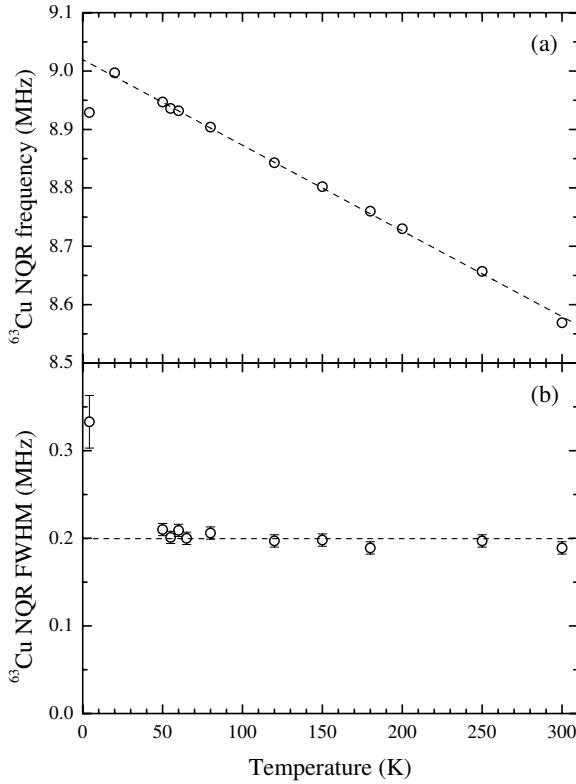


Figure 5: Symbols: (a)  $^{63}\text{Cu}$ -NQR frequency and (b) line-width of  $\text{PrCu}_2$  as a function of temperature, as obtained from the best-fits to the NQR spectra. The dashed lines represent (a) a linear fit and (b) the average of the data above 7 K.

small anisotropy of the thermal expansion coefficients.<sup>15</sup> Moreover no evidence of such a large variation can be inferred from the NMR data shown in fig. 1, because in the presence of a large  $\eta$  the edges of the quadrupolar wings are dramatically smeared out. It is therefore reasonable to ascribe most of the change in  $\nu_Q$  to a corresponding increase of  $V_{zz}$ , probably induced by the thermal contraction of the lattice.<sup>15</sup> The lack of any anomaly in  $\nu_Q(T)$  around 65 K does not add support to the magnetic-order scenario inferred from the  $\mu\text{SR}$  data.

Between room-temperature and  $T_{\text{JT}}$  the line-width  $\Gamma$  is almost constant. In particular, also  $\Gamma(T)$  exhibits no anomaly around 65 K. Likewise the absolute values of  $\Gamma$  are in contrast with a magnetic order of the Pr moments. Because of the interaction of the Pr-moments with the conduction electrons, magnetic order among them would imply a local field  $\vec{B}_{\text{Cu}}^{\text{hf}}$  acting on the Cu-sites. As discussed above (sect. III), the contribution to this field of any Pr moment oriented along  $a$  can be calculated by means of the corresponding hyperfine constant, i.e.  $B_{\text{Cu}}^{\text{hf}} = A_{aa}\mu_{\text{Pr}}$ . We calculated the local magnetic fields acting on Cu sites by invoking the six nearest-neighbors Pr moments, adopting the claimed AF configuration with an incommensurate modulation of the moments. The corresponding vector  $\vec{q} = (0.24, 0, 0.68)$  and the modu-

lation amplitude is  $0.29 \mu_B$ .<sup>10</sup> We obtain a distribution of  $B_{\text{Cu}}^{\text{hf}}$  ranging from 0 to  $0.06 \text{ T}$ . Such a distribution of fields should be reflected in a broadening  $\Delta\nu = 1.4 \text{ MHz}$  of the NQR line. This value is almost one order of magnitude larger than  $\Gamma$  of our signals, thus indicating that a magnetic order of the claimed type<sup>10</sup> is incompatible with our data.

Since the features extracted from the NQR spectra do not confirm, but rather rule out AF ordering of the Pr moments at 65 K, it seems in order to discuss possible causes for this discrepancy. At present we consider two scenarios which we discuss in more detail in section V. The first is based on the assumption that the apparent order observed with muons is mainly due to a muon-induced local enhancement of slow spin fluctuations. As a second possibility we consider that the observed order is not static, but fluctuates on a time-scale of the order of  $1 \mu\text{s}$ . With  $\mu\text{SR}$  and the related precession frequency of the order of  $10 \text{ MHz}$ ,<sup>10</sup> a non-zero field would be indicated. The characteristic time period in employing the NMR/NQR spin-echo technique are in the range of tens of microseconds and therefore the field fluctuations in the MHz range would be averaged to zero and thus would not affect the resonance signal. Under these circumstances,  $\mu\text{SR}$  would indicate a “static” magnetic correlation with a distribution of internal fields, whereas in NMR/NQR the fields would be averaged to zero. Such a slow dynamics has no simple explanation. Of course, the presence of a temporally fluctuating field should be reflected in the dynamical magnetic properties on a microscopic scale, namely the SLRR  $T_1^{-1}$  and the SSRR  $T_2^{-1}$ . At any rate, the onset of magnetic-order is, usually in the vicinity of the transition, accompanied by strong magnetic fluctuations, which should be reflected in the relaxation rates.

## B. Relaxation

With the procedures described in section II, we measured the time recovery of the longitudinal  $m_L(t)$  and transversal  $m_T(t)$  magnetization. Representative examples of  $m_L(t)$  and  $m_T(t)$  are shown in the insets of fig. 6(a) and (b), respectively. All the  $m_L(t)$  curves can be fitted by means of the standard exponential function that applies for  $I = 3/2$ ,<sup>16</sup> namely

$$m_L(t) = m_L(\infty) \left[ 1 - \exp \left( -\frac{\rho t}{T_1} \right) \right], \quad (6)$$

where  $m_L(\infty)$  is the equilibrium magnetization,  $T_1$  is the spin-lattice relaxation time, and  $\rho$  is an  $\eta$ -dependent parameter, which can be approximated with  $\rho \simeq 3$  for  $0 \lesssim \eta \lesssim 0.2$ .<sup>16</sup> Because the standard dipole-dipole interaction is not the main spin-spin relaxation mechanism,  $m_T(t)$  cannot be fitted by means of a simple exponential function. The stronger indirect interaction mediated by the conduction electrons via the Ruderman-Kittel-Kasuya-Yosida mechanism leads to a gaussian correction<sup>17,18</sup>

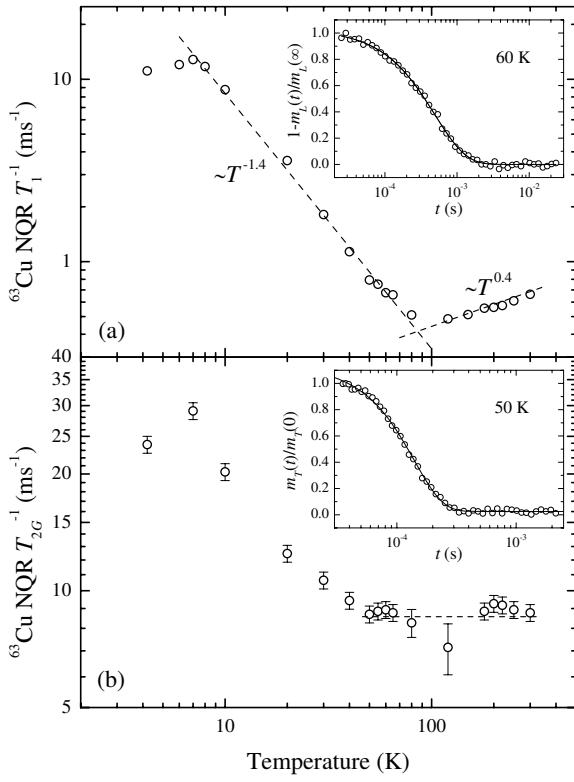


Figure 6: (a) Spin-lattice and (b) spin-spin relaxation rates as a function of temperature. Dashed lines in (a) are power-law fits to the data in the temperature range above and below 100 K. The uncertainty of the data points in (a) is of the order of the diameter of the open circles. The horizontal dashed line in (b) is a guide to the eyes. Insets: examples of the time dependent longitudinal (a) and transversal (b) magnetization. Solid lines in the insets of (a) and (b) are best fits to data according to equations 6 and 7, respectively.

such that

$$m_T(t) = m_T(0) \exp \left[ -\frac{t}{T_R} - \frac{1}{2} \left( \frac{t}{T_{2G}} \right)^2 \right], \quad (7)$$

where  $m_T(0)$  is the initial transverse magnetization,  $T_{2G}$  is the gaussian spin-spin relaxation time, and  $T_R = 3T_1/(2+r)$  is a time-scale depending on the SLRR and on its anisotropy  $r$ . Since this anisotropy is expected to be not as large as, e.g., in the layered copper oxides ( $r \sim 4$ ), we assume  $r \sim 1$  and hence  $T_R \sim T_1$ . As long as  $T_R$  is significantly larger than  $T_{2G}$ , their values are quite independent. Our assumption  $T_R = T_1$  is thus justified *a posteriori*, both by the good quality of the fits and by the fact that we obtain systematically  $T_{2G} < T_1$ .

From the fits based on equations 6 and 7, we obtain the temperature dependencies of the SLRR and SSRR, as shown in figs. 6(a) and (b), respectively. Neither  $T_1^{-1}(T)$  nor  $T_{2G}^{-1}(T)$  exhibit the expected features that would reflect an onset of magnetic-order around 65 K. The fluctuations that accompany such a transition should cause

a distinct enhancement of the relaxation rates, resulting in a peak in  $T_1^{-1}(T)$  around the ordering temperature. From fig. 6(b) we take it that  $T_{2G}^{-1}(T)$  is constant down to around 40 K where it starts to increase with decreasing temperature, displaying a peak at  $T_{JT}$ . The decrease of  $T_{2G}^{-1}(T)$  below  $T_{JT}$  most likely reflects the reduction of the quadrupolar fluctuations. Also  $T_1^{-1}(T)$  peaks at  $T_{JT}$ , but the behavior at higher temperature is more difficult to interpret. The temperature dependence of the SLRR is neither compatible with a dominating relaxation via conduction electrons ( $T_1^{-1}(T) \sim T$ ), nor a relaxation via local magnetic moments ( $T_1^{-1} = \text{const.}$ ) or by spin-wave type excitations ( $T_1^{-1} \sim T^3$ ). Instead  $T_1^{-1}(T)$  exhibits a power-law type behavior characterized by a negative exponent (-1.4) between 8 and 100 K and a positive one (0.4) above 100 K. In order to interpret this puzzling behavior, we tried to determine the leading spin-lattice relaxation mechanism by measuring  $T_1$  also for  $^{63,65}T_1$ ,  $^{63,65}\gamma$ , and  $^{63,65}Q$  we denote the spin-lattice relaxation time, the gyromagnetic ratio, and the quadrupole moment of  $^{63,65}\text{Cu}$ , respectively. If the dominant mechanism is magnetic,

$$^{63}T_1/^{65}T_1 = (^{65}\gamma/^{63}\gamma)^2 = 1.167, \quad (8)$$

whereas for a relaxation driven by the quadrupolar interaction we expect

$$^{63}T_1/^{65}T_1 = (^{65}Q/^{63}Q)^2 = 0.872. \quad (9)$$

We established that below 100 K  $^{63}T_1/^{65}T_1 \simeq 1.1$  which indicates that the relaxation is predominantly of magnetic origin. At higher temperature we find  $^{63}T_1/^{65}T_1 \simeq 1$ , suggesting that the magnetic and quadrupolar interactions are of comparable importance. The fact that the magnetic fluctuations dominate below 100 K again suggests that the internal field, if any is present, is not static. It is also worth mentioning that the puzzling  $T_1^{-1}(T)$  cannot be ascribed to the temperature dependence of the population of the Pr levels in simple terms. Such a case would require that the lifetimes of these levels are different for each of them. Bearing in mind the single-exponential behavior exhibited by all our  $m_L(t)$  curves, this possibility appears as rather unlikely.

## V. COMPARISON BETWEEN NMR/NQR AND $\mu$ S R MEASUREMENTS

Our *ab initio* calculations indicate that the dominant axis of the EFG and thus the quantization direction in NQR, is orthogonal to the  $a$  axis (see section III). If we assume that the internal field along  $a$  observed by  $\mu$ S R is not static but fluctuates, this would result in a large SLRR whereas it should have only minor effects on the SSRR. This is consistent with our observation that on decreasing the temperature,  $T_1^{-1}(T)$  increases much more rapidly than  $T_{2G}^{-1}(T)$ . As already mentioned (sect. IV A), this scenario could reconcile the NMR/NQR data with

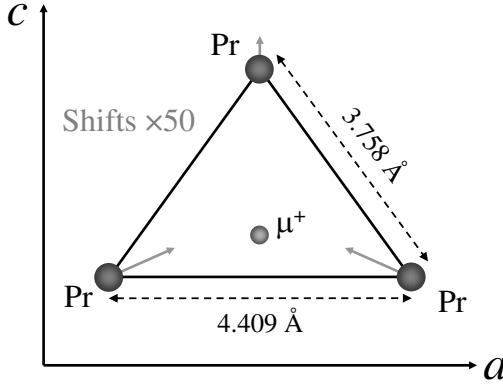


Figure 7: Sketch of the positions of the Pr ions surrounding the muon, as obtained from the *ab initio* calculations (see text). The arrows indicate the displacement of the Pr ions (multiplied by 50) induced by the presence of the muon.

the  $\mu$ SR results, provided that the time-scale of the spin polarization is long ( $\sim 1 \mu\text{s}$ ). This would also be consistent with the observation of a gaussian transverse relaxation, since the presence of such a term requires an enhancement of the low-frequency components of the local susceptibility,<sup>18</sup> i.e., a slowing down of the spin dynamics.

In order to reconcile the results of the NMR/NQR and  $\mu$ SR experiments, we also consider the possibility that the magnetic order observed by  $\mu$ SR is mimicked by a quasi-static local enhancement of moment polarization by the probe itself. The muon, considered as a positive point charge, will attract electrons and thus lead to a rearrangement of charge and possibly of the ion positions. If, because of a slow enough spin fluctuation, the intrinsic electronic charge distribution is spin polarized during the duration of the muon lifetime, the muon will experience a spin density exceeding the one induced by the fluctuation. For our calculations<sup>19</sup> we introduce a hydrogen atom<sup>20</sup> at the position of the muon derived by Schenck et al.  $(1/2, 1/4, 0.6406)^{10}$  in every second cell along the  $a$  direction, which amounts to one muon per 8 formula units, and let all atoms relax at fixed volume. The resulting coordinates for the position of the muon are  $(1/2, 1/4, 0.6465)$ , independent of the imposed spin polarization between 0 and  $1 \mu_B$  per unit cell. The Pr-ions in the nearest neighbor triangle are displaced as shown in fig. 7. The Pr-Pr distance is reduced by  $\sim 0.3\%$  which corresponds to a compression by approximately 5 kbar.<sup>21</sup> At this point, it is worth mentioning that at external pressures exceeding 12 kbar, AF ordering of the Pr moments has been observed for  $T \lesssim 9 \text{ K}$ ,<sup>21,22</sup> thus indicating that a lattice compression enhances the magnetic correlations. Imposing a spin polarization of  $1 \mu_B$  per unit cell, which corresponds to an average spin density of  $6.4 \cdot 10^{-4} \text{ a.u.}$ , leads to a spin density at the muon

site which is a factor 6.6 larger than the average one. Reducing the imposed spin polarization by a factor 4 yields a spin density at the muon 12 times larger than the average value. One might argue that the conclusions drawn from a calculation in which a hydrogen atom is placed in every second cell cannot be applied to the analysis of  $\mu$ SR experiments, which are performed with isolated muons. Our experience shows that if we double the number of hydrogens to one per cell, the enhancement of the spin density at the muon-site is reduced by 15%. In other words, a larger dilution is expected to enhance the influence of the muon. So there is no doubt that the presence of the muon affects the response of the system, namely a small spin polarization in the system will be amplified at the muon site. A quantitative assessment of the temperature dependence of this extrinsic effect is out of reach of the presently used calculation method.

## VI. CONCLUSIONS

The results of our NMR/NQR study of both the static (spectra) and dynamical (relaxation rates) microscopic magnetic properties of  $\text{PrCu}_2$  provide no evidence for the onset of any magnetic order around 65 K that was previously claimed from  $\mu$ SR data.<sup>10</sup> As argued above, the  $\mu$ SR results may not reflect magnetic order but are rather due to a muon-induced local enhancement of slow polarization fluctuations. If the fluctuation has a time scale of the order of  $1 \mu\text{s}$ , it could, as argued in section IV A, appear as static in  $\mu$ SR and vanishing in NMR/NQR. The origin of the anomalous power-law behavior of the SLRR is not yet understood, but it clearly indicates that the magnetic behavior of  $\text{PrCu}_2$  is far from that of a simple Pauli, Curie-Weiss type, or spin-wave system.

The present results call for further studies in order to clarify the complex magnetic properties of  $\text{PrCu}_2$ . In particular it will be important to carry out NMR/NQR measurements in an AF phase. This could be obtained either by means of measurements below 54 mK or at pressures exceeding 12 kbar, where AF ordering among localized Pr moments has been observed for  $T \lesssim 9 \text{ K}$ .<sup>21,22</sup>

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